

CLAIMS

1. An enzyme electrode comprising:
 - a portion of electrode formed on an insulating substrate;
 - 5 an immobilized enzyme layer formed over the portion of electrode;
 - an adhesion layer comprising a silane-containing compound formed over the immobilized enzyme layer; and
 - 10 a permeation-limiting layer comprising a fluorine-containing polymer having a structure where a pendant group containing at least a fluoroalkylene block is attached to an unfluorinated vinyl-based polymer, which is formed on the adhesion layer.
2. An enzyme electrode as claimed in Claim 1 wherein
15 said adhesion layer is a layer composed essentially of a silane coupling agent.
3. An enzyme electrode as claimed in Claim 1 or 2 wherein said fluorine-containing polymer is a fluoroalcohol ester of a polycarboxylic acid (A) in which the polycarboxylic acid (A)
20 is contained as the unfluorinated vinyl-based polymer thereof.
4. An enzyme electrode as claimed in Claim 1 or 2 wherein said fluorine-containing polymer is a mixture that contains a fluoroalcohol ester of a polycarboxylic acid (A) in which the polycarboxylic acid (A) is contained as the
25 unfluorinated vinyl-based polymer and additionally an alkylalcohol ester of a polycarboxylic acid (B).

5. An enzyme electrode as claimed in Claim 4 wherein said fluorine-containing polymer is a copolymer composed of said fluoroalcohol ester of the polycarboxylic acid (A) and the alkylalcohol ester of the polycarboxylic acid (B).

5 6. An enzyme electrode as claimed in Claim 4 or 5 wherein said polycarboxylic acid (B) is selected from polymethacrylic acid, polyacrylic acid or a copolymer of acrylic acid and methacrylic acid.

7. An enzyme electrode as claimed in any one of
10 Claims 3 to 6 wherein said polycarboxylic acid (A) is selected from polymethacrylic acid, polyacrylic acid or a copolymer of acrylic acid and methacrylic acid.

8. An enzyme electrode comprising:
a portion of electrode formed on an insulating
15 substrate;
an electrode protective layer covering the portion of electrode;
a binding layer comprising a silane-containing compound, which is formed on the electrode protective layer;
20 an ion-exchange resin film layer formed on the binding layer;
an immobilized enzyme layer formed on the ion-exchange resin film layer;
an adhesion layer comprising a silane-containing compound, which is formed on the immobilized enzyme layer;
25 and

a permeation-limiting layer comprising a fluorine-containing polymer having a structure where a pendant group containing at least a fluoroalkylene block is attached to an unfluorinated vinyl-based polymer, which is formed on the
5 adhesion layer.

9. An enzyme electrode as claimed in Claim 8 wherein said electrode protective layer is made essentially of a urea compound.

10. An enzyme electrode as claimed in Claim 8 wherein said binding layer and said adhesion layer are layers composed essentially of a silane coupling agent.

11. An enzyme electrode as claimed in Claim 8 wherein said fluorine-containing polymer is a fluoroalcohol ester of a polycarboxylic acid (A) in which the polycarboxylic acid (A) is contained as the unfluorinated vinyl-based polymer thereof.
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12. An enzyme electrode as claimed in Claim 8 wherein said fluorine-containing polymer is a mixture that contains the fluoroalcohol ester of the polycarboxylic acid (A) in which the polycarboxylic acid (A) is contained as the unfluorinated
20 vinyl-based polymer and additionally an alkylalcohol ester of a polycarboxylic acid (B).

13. An enzyme electrode as claimed in Claim 12 wherein said fluorine-containing polymer is a copolymer composed of said fluoroalcohol ester of the polycarboxylic acid
25 (A) and the alkylalcohol ester of the polycarboxylic acid (B).

14. An enzyme electrode as claimed in Claim 12 or 13

wherein said polycarboxylic acid (B) is selected from polymethacrylic acid, polyacrylic acid or a copolymer of acrylic acid and methacrylic acid.

15. The enzyme electrode as claimed in any one of
5 Claims 11 to 13 wherein said polycarboxylic acid (A) is selected from polymethacrylic acid, polyacrylic acid or a copolymer of acrylic acid and methacrylic acid.

16. An enzyme electrode comprising:
a portion of electrode formed on an insulating
10 substrate;
an immobilized enzyme layer formed on the portion
of electrode; and
a permeation-limiting layer formed over the
immobilized enzyme layer and placed on the uppermost surface;
15 wherein said permeation-limiting layer consists of a
film essentially comprising a fluorine-containing polymer, and
many grooves are built in on the surface of said
permeation-limiting layer consisting of the film essentially
comprising a fluorine-containing polymer.

20 17. An enzyme electrode as claimed in Claim 16
wherein an average thickness of said permeation-limiting layer
is selected within a range of 0.01 to 1 μm ; and the surface of
the permeation-limiting layer has an irregular shape having a
surface roughness within a range of 0.0001 or more and 1 or
25 less fold of said average thickness of the permeation-limiting
layer.

18. An enzyme electrode as claimed in Claim 16
wherein said fluorine-containing polymer is a polymer having a
structure where a pendant group containing at least a
fluoroalkylene block is attached to an unfluorinated vinyl -based
5 polymer.

19. An enzyme electrode as claimed in Claim 16 or 18
wherein said fluorine-containing polymer is a fluoroalcohol ester
of a polycarboxylic acid (A) in which the polycarboxylic acid (A)
is contained as the unfluorinated vinyl -based polymer thereof.

10 20. An enzyme electrode as claimed in Claim 16 or 18
wherein said fluorine-containing polymer is a mixture that
contains the fluoroalcohol ester of the polycarboxylic acid (A) in
which the polycarboxylic acid (A) is contained as the
unfluorinated vinyl-based polymer and additionally an
15 alkylalcohol ester of a polycarboxylic acid (B).

21. An enzyme electrode as claimed in Claim 20
wherein said fluorine-containing polymer is a copolymer
composed of the fluoroalcohol ester of the polycarboxylic acid
(A) and the alkylalcohol ester of the polycarboxylic acid (B).

20 22. An enzyme electrode as claimed in Claim 20 or 21
wherein said polycarboxylic acid (B) is selected from
polymethacrylic acid, polyacrylic acid or a copolymer of acrylic
acid and methacrylic acid.

23. An enzyme electrode as claimed in any one of
25 Claims 19 to 21 wherein said polycarboxylic acid (A) is selected
from polymethacrylic acid, polyacrylic acid or a copolymer of

acrylic acid and methacrylic acid.

24. A process for manufacturing an enzyme electrode comprising the steps of:

- forming an electrode film on the main surface of an insulating substrate and then patterning the electrode film to form a plurality of portions of electrodes;
 - forming an electrode protective layer covering the electrode surface;
 - forming a binding layer comprising a silane-containing compound on the main surface of the insulating substrate;
 - forming an ion-exchange resin film layer on the main surface of the insulating substrate;
 - applying a liquid containing an enzyme to the main surface of the insulating substrate and then drying the insulating substrate to form an immobilized enzyme layer;
 - applying a liquid containing a fluorine -containing polymer having a structure where a pendant group comprising at least a fluoroalkylene block is attached to an unfluorinated vinyl-based polymer to the main surface of the insulating substrate by spin coating and then drying the insulating substrate to form the permeation-limiting layer; and
 - dicing the insulating substrate to give a plurality of enzyme electrodes.
25. An process for manufacturing an enzyme electrode as claimed in Claim 24 wherein the process is performed in

such manner where after said step of forming the immobilized enzyme layer, further step of applying a liquid comprising a silane-containing compound to the main surface of the insulating substrate and then drying the insulating substrate to

5 form an adhesion layer is carried out, and followed by the step of applying the liquid containing said fluorine -containing polymer to the upper surface of the adhesion layer coating the main surface of the insulating substrate and then drying the insulating substrate to form the permeation-limiting layer,

10 26. An process for manufacturing an enzyme electrode as claimed in Claim 24 or 25 wherein said permeation-limiting layer is a layer being formed by spin coating.

27. An process for manufacturing an enzyme electrode as claimed in Claim 25 wherein said silane-containing compound used for forming the adhesion layer is a silane coupling agent.

15 28. A biosensor comprising an enzyme electrode as claimed in any one of Claims 1 to 23.

29. An process for manufacturing an enzyme electrode as claimed in Claim 24 or 25 wherein said fluorine-containing polymer is a polymer having a structure where a pendant group containing at least a fluoroalkylene block is attached to an unfluorinated vinyl-based polymer.

30. An process for manufacturing an enzyme electrode as claimed in any one of Claims 24, 25 and 29 wherein said fluorine-containing polymer is a fluoroalcohol ester of a

polycarboxylic acid (A) in which the polycarboxylic acid (A) is contained as the unfluorinated vinyl -based polymer thereof.

31. An process for manufacturing an enzyme electrode as claimed in any one of Claims 24, 25, 29 and 30 wherein said 5 fluorine-containing polymer is a mixture that contains the fluoroalcohol ester of the polycarboxylic acid (A) in which the polycarboxylic acid (A) is contained as the unfluorinated vinyl-based polymer and additionally an alkylalcohol ester of a polycarboxylic acid (B).

10 32. An process for manufacturing an enzyme electrode as claimed in Claim 32 wherein said fluorine-containing polymer is a copolymer of said fluoroalcohol ester of the polycarboxylic acid (A) and the alkylalcohol ester of the polycarboxylic acid (B).

15 33. An process for manufacturing an enzyme electrode as claimed in Claim 31 or 32 wherein said polycarboxylic acid (B) is selected polymethacrylic acid, polyacrylic acid or a copolymer of acrylic acid and methacrylic acid.

34. An process for manufacturing an enzyme electrode 20 as claimed in any one of Claims 30 to 32 wherein said polycarboxylic acid (A) is selected from polymethacrylic acid, polyacrylic acid or a copolymer of acrylic acid and methacrylic acid.